FINAL TECHNICAL REPORT

Award Number:	DE-FG36-04GO14317
Project Title:	New Sustainable Chemistry for Adhesives, Elastomers and Foams
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DISCLAIMER

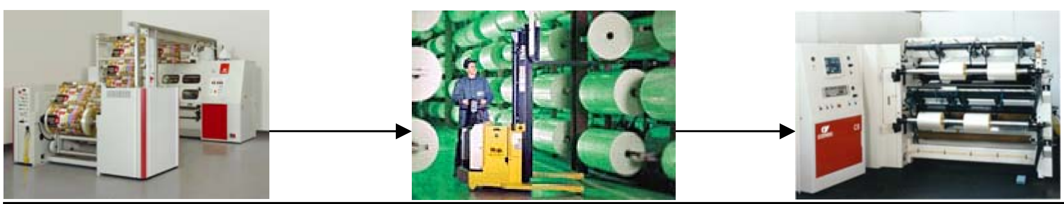
EXECUTIVE SUMMARY

Introduction

The overall U.S. market size for all polyurethane adhesives is estimated to be 92.2 MM lbs in 2005 and growing at 12% per year. The total U.S. market for all adhesive, foam and elastomer applications was estimated to be 5.5 billion lbs in 2005. This 2-year program focused on the research and development of new biobased, non-isocyanate based chemistries to replace existing 2-part polyurethane adhesives for various uses including flexible packaging. The work was extended to research the technical feasibility of developing biobased, non-isocyanate-based foams and elastomers.

Goal- Biobased Adhesives

Despite extraordinary acceptance in a wide variety of markets, polyurethane chemistry has deficiencies. The raw materials (isocyanates) must be handled properly to avoid sensitizing workers. Additionally, isocyanates and polyols are petroleum-derived and hence non-renewable. Furthermore, in some flexible film adhesive applications for food packaging, aromatic isocyanate components can react with water to form aromatic amines which are suspected carcinogens. This by-product formation requires additional safeguards which result in increased work-in-process and inventory before slitting and shipment to end-users can be accomplished.



The process of coating, curing in inventory and slitting for shipment may take 3-7 days with polyurethanes

Our project focused on the goal of providing commercially-viable adhesives for flexible packaging (primary) and structural (secondary) that exhibit equivalent performance to that of polyurethanes yet with the advantages of:

a) faster cure thereby reducing the working capital and increasing production agility;
b) elimination of the handling of isocyanates in adhesive production;
c) elimination of the handling of isocyanates in production facilities using adhesives;
d) elimination of aromatic amine formation in food packaging;
e) increased price stability due to lessened dependence on petrochemical feedstock;
f) reduced greenhouse gas emissions.

A secondary goal was to extend the research to determine the technical feasibility of developing bio-based, non-isocyanate-based foams and elastomers with many of the same expected benefits as for adhesives.

Polyurethane adhesives utilize methylene diisocyanate (MDI) with various petrochemical-derived polyols (polyesters and polyethers). MDI is a known chemical sensitizer. Solventless polyurethane adhesives are typically two-part systems in which one part (A) contains an isocyanate-based pre-polymer derived from MDI and the second part (B) is a hydroxyl-containing pre-polymer or polyol. Polyurethane foams and elastomers are closely related technologically to polyurethane adhesives and, not surprisingly, share common raw materials.

This project utilized Carbon Michael chemistry, a non-isocyanate technology, in which the reactants, which are bio-based, form polyester compositions which rival polyurethanes in performance. The work initially involved synthesis of bio-based reactants, such as acetoacetates and acrylates of a mono- or disaccharides and other bio-based materials such as castor oil, glycerol, and crop oil derivatives. These reactants were then formulated at levels from 20-60% to produce non-isocyanate bio-based adhesives, foams, and elastomers. Proprietary, low toxicity catalysts were used to promote the reaction. Desirable bio-based reactants were then scaled-up to pilot plant scale. The hazards associated with acetoacetates and the acrylates chosen for the work were demonstrated to be lower than those for MDI based reactants.

A moderate level (approximately 20% overall market penetration) of success with this technology is expected to lead to the replacement of >100 MM lbs of petrochemical-based materials with materials derived from biomass. The projected impact of this on the rural economy is estimated to be $124 million per year in added return to farmers assuming consumption of 50 million lb of soybean oil used. (Recently available figures, i.e. 2003, place the total US production of soybean oil at 16.3 trillion lbs). The use of soybean oil in place of petroleum derived chemicals will sequester 138 million pounds of greenhouse gases each year.

Accomplishments

1. Synthesis and characterization of over 50 bio-based raw materials were conducted in Rohm and Haas' Spring House, PA laboratories to determine the most suitable candidates for the various applications.
2. Advice on the future supply and cost projections of various biorefinery outputs was received from Dr. Thomas A. Foglia of the USDA Eastern Regional Research Center in Wyndmoor, PA to guide the bio-based raw material selection process.
3. Extensive toxicology testing was carried out at contract laboratory facilities on a preferred raw material, glycerol tris acetoacetate, to ensure a low toxicity profile and to allow formal submission to the EPA for TSCA listing. These data may also be useful for future TSCA submissions on related biobased acetoacetates.
4. Rohm and Haas applied to the US EPA for the TSCA listing of glycerol tris acetoacetate. The EPA has issued a Consent Order to allow limited commercial use of the material, pending the completion of additional toxicity testing, based on the relatively low hazard level of the material.
5. Formulation optimization and extensive end-use testing have resulted in several adhesive prototypes for the flexible packaging market, These rival the performance of 2-part polyurethanes. One key performance attribute, however, was still deficient and was not satisfactorily resolved by the completion of funding. Similar work on structural adhesives also resulted in interesting

prototypes with performance rivaling that of polyurethanes. However, the prototypes could not match the performance of epoxies.

6. Raw material specifications were established for glycerol tris acetoacetate and communicated to two potential suppliers. Scale-up of glycerol tris acetoacetate and other preferred raw materials has taken place to allow sufficient materials for customer trials and in-house high-line-speed optimization trials.
7. High-line-speed trials of optimized formulations for flexible laminating were conducted at Rohm and Haas' Ringwood, IL facility using several bio-based non-isocyanate prototypes for lead customer qualification. Excellent coating quality, clean processing and acceptable cure rate were observed on key substrate combinations during these runs.
8. Commercialization of bio-based flexible packaging adhesives has been delayed due to a shortcoming in one key performance test. Work is ongoing beyond the scope of the DOE funded work to resolve these issues and to reintroduce an improved version of the product when appropriate.
9. Commercialization of bio-based structural adhesives has been abandoned for the present time, despite solid technical results, due to an unattractive value proposition.
10. Technical feasibility of technology for foams and elastomers was established. The former work was done at Rohm and Haas' Spring House, PA research facility while the latter was carried out at Virginia Tech in Blacksburg, VA under the direction of Dr. Timothy E. Long.
11. Two US patent applications were filed and a total of 15 concept documents (indicating patentable inventions) were created and communicated to the DOE over the course of the 2 year project.

Project Objective:
The goal of the project was to research and develop a biorefinery technology platform for adhesives, elastomers and foams. The platform is based on renewable feedstocks including derivatives of sugars and modified crop oils. The program was to develop new bio-based products which can replace petrochemical-based polyurethane technology in film laminating and other adhesive, sealant and elastomer applications. The technology provides productivity (faster cure and lower energy consumption) and safety (lower toxicity profile) enhancements versus incumbent polyurethane technology.

Background:
This project was undertaken in response to the U. S. Department of Agriculture's and the U. S. Department of Energy's solicitation "to promote greater innovation and development related to biomass and to support Federal policy calling for greater use of biomass-based products, feedstock production and processing conversion."[1]

The project pursued a biorefinery approach to produce novel soy-sugar polymers. The program developed new products which can replace petroleum-based polyurethane adhesives, elastomers and foams. The program yielded technologies which provide a range of specific performance, safety and economic advantages over polyurethanes including faster cure allowing reduced working capital and increased production agility; elimination of isocyanate handling in production and use of adhesives; elimination of aromatic amine formation in food packaging; increased price stability through reduced dependence on petroleum feedstocks; and reduced greenhouse gas formation. Ultimately, it offers the potential to replace the use of >100 million lbs of petroleum-based materials with those derived from plants, thus sequestering 138 million pounds of greenhouse gases each year. The project was initially slated to cover two years and cost a total of $2.89 million, 31 percent of which was to come from Rohm and Haas Company. The project actually ran for 26 months with a total cost of $2.936M with the DOE portion remaining $2M. The additional cost share by Rohm and Haas was required for unanticipated toxicological testing required for TSCA compliance and Rohm and Haas' internal safety assessment as well as for on-going efforts to improve a key performance shortcoming of the flexible laminating adhesive prototypes.

This novel adhesive technology is based on the (Carbon) Michael reaction of an active hydrogen nucleophile (**Nu:**) (or donor) with a multi-functional acrylate electrophile (or acceptor) in the presence of proprietary basic catalysts **(Figure 1)**. The nucleophile is a deprotonated acetoacetate of any of a variety of polyols. This technology, although well-known academically, had never been exploited industrially for adhesive applications. Moreover, extension of the technology to uses for foams and elastomers was also never practiced induistrially. Prior to obtaining funding for the bio-based Carbon Michael program, Rohm and Haas had demonstrated the commercial viability of Carbon Micahel chemistry to make commercially-viable adhesives for flexible laminating using **petroleum-derived reactants**.

[1] Financial Assistance Announcement of Funding Opportunity, Biomass Research and Development Initiative DE-PS36-04GO94002, p. 1.

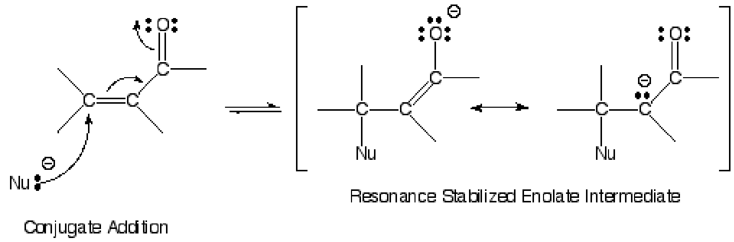


Figure 1

The goal of the DOE funded program was to make acetoacetates and acrylates derived from **bio-based polyols** and to carry out reactions to produce adhesives, foams and elastomers that function as well as polyurethanes, yet with added value. The synthesis of the bio-based derived acetoacetates has been accomplished by Rohm and Haas using transesterification (with t-butyl acetoacetate) at the lab scale. Figure 2 shows the transesterification reaction using isosorbide as the alcohol and t-butyl acetoacetate (TBAA). Commercial production of the acetoacetates will most likely utilize the lower cost direct reaction with diketene which has no by-product formation.

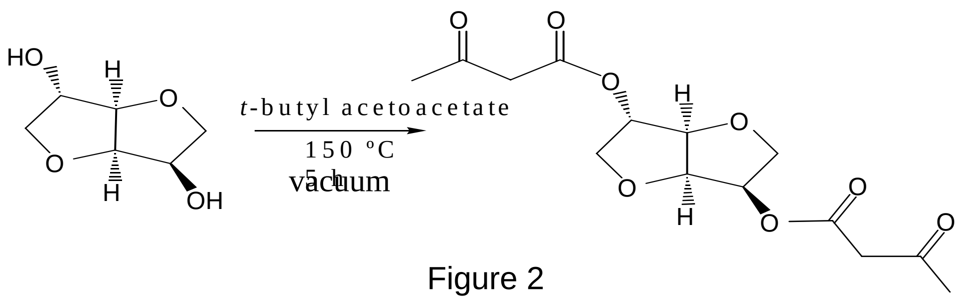


Figure 2

The project addressed the following key tasks and milestones:

Task 1 involved the synthesis and characterization of bio-based reactants and polymers. The objective was to be to develop starting materials from sugars and crop oils (see Figure 3 for some preferred starting materials) which react to form polymers suitable for adhesive, elastomer and foam applications. An important outcome of this task was the Structure/Property Relationships to guide product development. Initial efforts focused on materials for adhesives. Later work focused on materials for foams and elastomers.

Tasks 2 and 3 involved developing new bio-based products for selected adhesive applications which provide a range of advantages over petroleum-derived polyurethanes. The team evaluated prototype products under laboratory and simulated industrial conditions to identify product formulations for scale-up and subsequent commercialization. Trials with selected customers verified value-in-use.

Task 4 involved development of the process for the manufacture of bio-based reactants. In addition, the team scaled-up adhesive products to commercial production scale which was targeted to occur by September 2006 if feedback was positive.

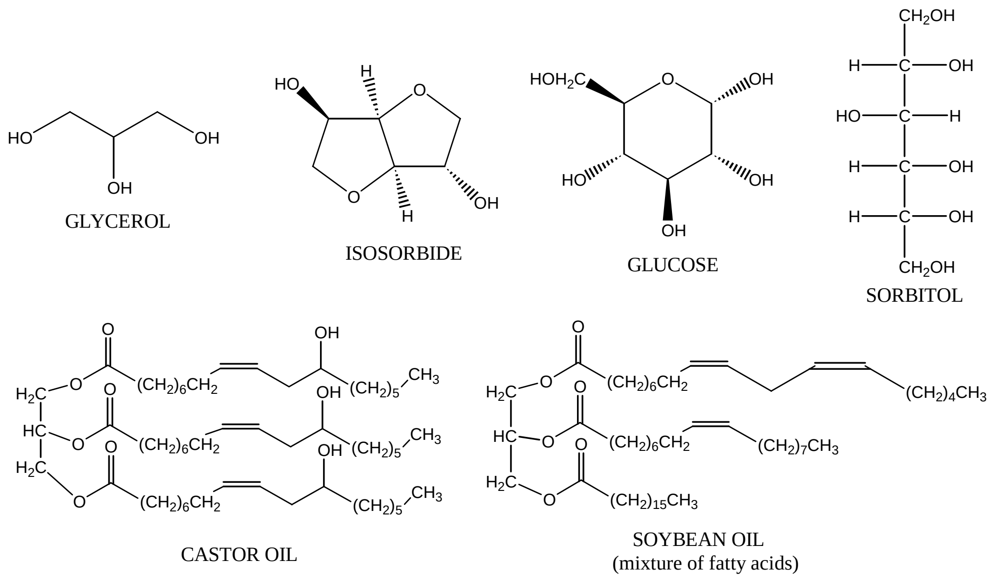


Figure 3

The final phase of the project (Task 5) was to assess bio-based polymers for potential use in foams and elastomers. In Task 5, the Structure/Property Relationships, developed in Task 1, were employed to identify candidate polymers for target applications.

The revised dates for Accomplishing Major Milestones are shown in the following table.

Major Milestone/Deliverable		**Date Month/Yr**
Laboratory synthesis and characterization of sugar and crop oil derivatives for adhesives completed.		3/05
Laboratory synthesis and characterization of sugar and crop oil derivatives for elastomers/foams completed.		9/05
Structure Activity Roadmaps completed.		9/05
Flexible Laminating Adhesive prototypes identified.		7/05
Flexible Laminating Adhesive prototypes finalized.		11/05
Flexible Laminating Adhesive product developed. Includes candidate formulations, internal and customer line trials, and toxicity assessment.		10/06
Flexible Laminating Adhesive product commercialized – first customer sales.		6/07*
Assembly Adhesive prototypes finalized.		3/06
Assembly Adhesive product developed.		9/06
Assembly Adhesive product commercialized – first customer sales.		NA
Candidate elastomer and foam polymers identified.		9/06

*This milestone was delayed beyond the scope of the project as a result of lengthy supply contract negotiations for a key raw material and, as a result, a delay in the signing of the EPA Consent Order by our supplier. It was also impacted by inadequate performance on critical substrate for a lead customer.

Discussion:
Quarterly meetings were held with the extended team (Virginia Tech, USDA ERRC) throughout the program to provide technical updates; assess progress against milestones; review timelines; and delineate any patentable concepts. Separate meetings were held with the EPA on the TSCA status of glycerol tris acetoacetate, contract labs, and with potential suppliers of key raw materials.

Task 1) Synthesis and characterization of bio-based reactants and candidate polymers.

Synthesis and characterization of over 50 bio-based raw materials were conducted in Rohm and Haas' Spring House, PA laboratories to determine the most suitable candidates for the various applications. Advice on the future supply and cost projections of various biorefinery outputs was received from Dr. Thomas A. Foglia of the USDA Eastern Regional Research Center in Wyndmoor, PA to guide the bio-based raw material selection process.

Extensive toxicology testing was carried out at contract laboratory facilities on a preferred raw material, glycerol tris acetoacetate, to ensure a low toxicity profile and to allow formal submission to the EPA for TSCA listing. These data may also be useful for future TSCA submissions on related bio-based acetoacetates for these and related applications. Other preferred raw materials from the work include epoxidized soy acrylate, isosorbide acetoacetate, and castor oil acetoacetate.

Rohm and Haas applied to the US EPA for the TSCA listing of glycerol tris acetoacetate. The EPA issued a Consent Order to allow limited commercial use of the material pending the completion of additional toxicity testing based on the relatively low hazard level of the material. This Consent Order document needs to be signed by the supplier identified in the document to allow commencement of commercial use of the material. At the time of writing this report, this identified supplier had not yet signed this document because a supply agreement has not yet been finalized. In the meantime, all required toxicology testing has been completed and is being sent to the EPA for review. If the EPA should deem the data acceptable and places no additional restrictions on the material, then commercial use can begin in the U.S. with any of a number of suppliers.

<u>Task 2). Flexible Laminating Adhesive Product Development</u>
Bio-based flexible packaging adhesive prototypes have exhibited excellent dry adhesion to a wide variety of film substrates as noted below (see Table 1). An especially interesting development was the excellent dry and wet adhesion results of the technology (TK 12-113-1 and related formulations) to various films (Table 2).

Prototype KMM 3-8-4 demonstrated very good performance in films of interest and was chosen as the first bio-based prototype to introduce to our lead customer in July 2005 (Table 3). These high-line-speed trials of optimized formulations for flexible laminating were conducted at Rohm and Haas' Ringwood, IL facility using several bio-based non-isocyanate prototypes for lead customer qualification. Excellent coating quality, clean processing and acceptable cure rate were observed on key substrate combinations during these runs.

Table 1

	Prototype 79106-72-4
Viscosity (45C)	1200 cps
Pot-life (45C)	18 min
Adhesion (T-peel)	
PET/foil	
24 hrs	715 g/in
7 days	581 g/in
PET/PE	
24 hrs	423 g/in
7 days	420 g/in
Printed PET(ink)/PE	
3 days	220 g/in -light blue
3 days	250 g/in -white

Table 2

	Prototype TK 12-113-1
Viscosity (35C)	2040 cps
Pot-life (35C)	30 min
Adhesion (T-peel)	
Polyester/LDPE	
5 days RT	432 g/in
2 days RT, 3 days 45C	1207 g/in
2 days RT, 3 days 45C 1 day water	241 g/in

Table 3

	Prototype KMM 3-8-4
Biobased content	>50%
Viscosity (45C)	1300 cps
Pot-life (45C)	18 min
Adhesion (T-peel)	
PET/PE	
24 hrs	513 g/in
48 hrs	793 g/in

Additionally, other necessary performance attributes for flexible laminating adhesives, such as manageable viscosity and pot-life, were achieved with numerous bio-based flexible packaging adhesive prototypes. Also, rapid cure on a variety of inks has been achieved. The limiting performance attribute for the technology in flexible packaging has been wet adhesion to some films and, as a result, inferior pasteurization resistance. It was recognized, during year 1 of the program, that wet adhesion was acceptable to some coated films, but such coated films are limited in use and, hence, not sufficient to propel the program to full commercialization.

An improved water resistance general purpose flexible laminating adhesive prototype was identified and was trial coated on the lead customer's substrates in early

November, 2006. Specifically, 79561-95-4 yielded excellent bond performance to several key substrate combinations, cured well on ink, and gave improved water soak resistance as compared to earlier prototypes. The coated substrates from the November line trial, however, were tested by the lead customer to confirm performance improvements. The results, however, still did not meet their requirements (in wet adhesion-one key performance attribute) to move into expanded commercialization.

Work, however, has continued beyond the DOE funding period and, as of March 2007, promising results have been obtained in wet adhesion based on a recent breakthrough. Work will continue through April/May 2007, after which, a decision will be made as to whether or not to reintroduce the technology to lead customers.

Commercialization efforts have also been frustrated by lengthy supply contract negotiations for a key raw material and, as a result, a delay in the signing of the EPA Consent Order by our supplier. The supplier will not sign the Consent Order until a contract is in place. The supply contract discussions continue and we anticipate completion of the agreement and the signing of the Consent Order during April.

<u>Task 3). Assembly Adhesive Prototype Development</u>

Several promising candidates that match the performance of existing commercial polyurethanes for some applications have been developed (see Table 4). Efforts to match epoxy performance have not been as successful. Without a clear, unique performance advantage against polyurethanes and a higher overall cost, this work has been de-emphasized to place more focus on flexible packaging. It is very doubtful that a commercially-viable assembly adhesive will be made available in the near future.

Table 4

Substrates	Prototype Biobased (>60%)	Commercial 2 part polyurethane adhesive
Wood to wood	520 psi (destruct)	566 psi (destruct)
Wood to primed metal	535 psi (destruct)	579 psi (destruct)
Wood to FRP plastic	232 psi	252 psi (destruct)
FRP to FRP	208 psi	256 psi (destruct)
Primed metal to primed metal	440 psi	597 (destruct)

<u>Task 4) Scale-up of Biomass-based Raw Materials</u>

A preferred catalyst and level of use for the production of glycerol tris acetoacetate were identified. Specifications have been finalized based on this work. Supply agreements with key suppliers are being finalized.

Upon receipt of the finalized toxicological and physical chemical data on glycerol tris acetoacetate (data on the last remaining study is anticipated shortly), Rohm and Haas may consider submitting a consolidated PMN to the EPA for additional bio-based acetoacetates. Any future consolidated PMNs may use the data collected on glycerol tris acetoacetate as a surrogate for the class of materials.

Task 5. Elastomer and Foam Feasibility Research

Work has validated the technical feasibility of making bio-based foams based on this technology platform. It appears such materials are technologically feasible based on formation of closed cell structure, improved water resistance, low density, and strength comparable to polyurethanes.

Work at Virginia Tech also established the technical feasibility of making elastomers based on this technology. An emphasis on increasing hydrogen bonding and optimizing polymer architecture has resulted in prototypes with the required combination of stress-at-break and percentage of elongation.

Intellectual Property

A total of 15 invention disclosures was submitted to Rohm and Haas patent attorney, Stephen Falk, and two patent applications were filed over the course of this program. The US DOE was separately informed of all such disclosures and patent applications by Stephen Falk.

Task Schedule

Task No.	Title/Task Description	Task Completion Date				Progress Notes
		Original Planned	Revised Planned	Actual	Percent Complete	
1	Synthesis and characterization of biobased reactants and candidate polymers.	2/06	N.A.		100%	A variety of bio-based acetoacetates and acrylates synthesized
2	Flexible Laminating Adhesive product development.	9/06	N.A.		100%	Formulations containing bio-based reactants demonstrate commercial viability technically and economically. One key performance attribute needs improvement for commercial success.
3	Assembly Adhesive product development.	9/06	N.A.		60%	Formulations containing bio-based reactants demonstrate commercial viability technically but not economically.
4	Manufacturing process optimization.	9/06	N.A.		90%	Lab synthesis conducted, scale-up of raw materials and catalysts achieved. Awaiting full TSCA listing key raw material and for supply agreement to be finalized.
5	Candidate polymers for other target applications including elastomers and foams identified	9/06	N.A.		100%	Lab synthesis conducted. Prototypes developed that meet targeted technical requirements for feasibility.

7. Future Plans

- Continue qualification of bio-based adhesive at flexible packaging customers beyond the scope of the DOE funding.